Journal of Asian Ceramic Societies 3 (2015) 266–270

HOSTED BY

Contents lists available at ScienceDirect

Journal of Asian Ceramic Societies

journal homepage: www.elsevier.com/locate/jascer

Fabrication of ITO particles using a combination of a homogeneous precipitation method and a seeding technique and their electrical conductivity

Yoshio Kobayashi [a,*], Naomichi Takahashi [a], Takafumi Maeda [a], Takehiro Yonezawa [b], Kazuhiko Yamasaki [b]

[a] Department of Biomolecular Functional Engineering, College of Engineering, Ibaraki University, 4-12-1 Naka-narusawa-cho, Hitachi, Ibaraki 316-8511, Japan
[b] Central Research Institute, Mitsubishi Materials Corporation, 1002-14 Mukohyama, Naka, Ibaraki 311-0102, Japan

ARTICLE INFO

Article history:
Received 26 February 2015
Received in revised form 20 April 2015
Accepted 19 May 2015
Available online 9 June 2015

Keywords:
Indium tin oxide
Particles
Homogeneous precipitation method
Seeding technique
Electric conductivity

ABSTRACT

The present work proposes a method to fabricate indium tin oxide (ITO) particles using precursor particles synthesized with a combination of a homogeneous precipitation method and a seeding technique, and it also describes their electronic conductivity properties. Seed nanoparticles were produced using a co-precipitation method with aqueous solutions of indium (III) chloride, tin (IV) chloride aqueous solution and sodium hydroxide. Three types of ITO nanoparticles were fabricated. The first type was fabricated using the co-precipitation method (c-ITO). The second and third types were fabricated using a homogeneous precipitation method with the seed nanoparticles (s-ITO) and without seeds (n-ITO). The as-prepared precursor particles were annealed in air at 500 °C, and their crystal structures were cubic ITO. The c-ITO nanoparticles formed irregular-shaped agglomerates of nanoparticles. The n-ITO nanoparticles had a rectangular-parallelepiped or quasi-cubic structure. Most s-ITO nanoparticles had a quasi-cubic structure, and their size was larger than the n-ITO particles. The volume resistivities of the c-ITO, n-ITO and s-ITO powders decreased in that order because the regular-shaped particles were made to strongly contact with each other.

1. Introduction

Tin-doped indium oxide, or indium tin oxide (ITO), is the most representative among transparent electro-conductive materials used for opto-electronic devices such as displays, solar cells and sensors [1–6]. ITO films can be produced using various methods such as electron beam evaporation, PVD, sputtering, CVD and spray [5,7–15]. Although these methods are conventionally used and fundamentally and industrially studied, they have some disadvantages as follows. Because the PVD and sputtering methods are used at low pressure, their instruments require a large and costly vacuum system. For the CVD and spray methods, the as-prepared ITO films on the substrate must be annealed at high temperature during or after preparation, which thermally damages the substrate if its material is sensitive to high temperature, such as plastics.

Coating the substrate with a colloid solution that contains ITO crystalline particles is an alternative method to produce ITO films [16–18]. Because the coating method uses the crystallites, the film is not required to be annealed for crystallization. Consequently, the substrate is not thermally damaged. Methods to produce a large amount of ITO crystalline particles at low cost with low environmental load chemicals are industrially required. From this viewpoint, the methods with aqueous solution that contains inorganic salts as the main precursors, i.e., aqueous-phase methods using inorganic salts, are promising.

ITO crystalline particles can be synthesized from aqueous solutions of inorganic salts with methods such as a sol–gel method [19–23], a co-precipitation method [24–28], and a hydrothermal and solvothermal process [29,30,28], which are representative among the aqueous-phase methods. The hydrothermal and solvothermal process can be extended to production of ITO-related compounds such as InOOH and $In(OH)_3$ [31–35]. A homogeneous

* Corresponding author. Tel.: +81 294 38 5052; fax: +81 294 38 5078.
E-mail address: ykoba@mx.ibaraki.ac.jp (Y. Kobayashi).
Peer review under responsibility of The Ceramic Society of Japan and the Korean Ceramic Society.

http://dx.doi.org/10.1016/j.jascer.2015.05.006

precipitation method is an alternative method as the aqueous-phase method. In the homogeneous precipitation method, precipitators such as urea are decomposed at high temperature, which slowly and homogeneously increase the solution pH. As a result, fine metal compound nanoparticles are produced. The precipitation method using the thermal decomposition of precipitator like the homogeneous precipitation process in an aqueous solution with dissolved indium salt and tin salt can be used for fabricating ITO crystalline particles [36,37]. The homogeneous precipitation method has an advantage over the other methods. Because the particles are homogeneously produced in the solution due to the thermal decomposition of precipitator, they are mono-dispersed, which indicates that all particles should have almost identical properties. Therefore, ITO films composed of the ITO crystalline particles that are fabricated using the homogeneous precipitation method may have reliable electric conductivity.

Our research group have studied the effects of nanocrystallite seeding on various oxides such as lead zirconate titanate, barium strontium titanate and alumina, which were fabricated using the sol–gel method in the last decade [38–43]. Their crystallization temperatures were decreased with the seeding. Surface of the seed nanocrystallites was considered to promote crystal growth. Accordingly, the presence of seed crystalline particles in the homogeneous precipitation also may increase crystallinity of ITO particles obtained from precursor particles produced with the homogeneous precipitation. If nuclei of precursor particles are generated in a reaction of raw chemicals in the presence of seed crystalline particles, the nuclei are deposited preferably on the seed crystalline particle surfaces. This means that shape of the seed crystalline particles is reflected by final ITO particles, which indicates that the seeding can vary the shape of the final ITO crystalline particles, and consequently affects electrical properties of ITO films composed of the ITO crystalline particles.

The aim of the present work is to propose a method for fabricating ITO crystalline particles from precursor particles synthesized using a combination of the homogeneous precipitation method and the seeding. Both advantages of the two processes are expected to be reflected for the fabricated particles. Consequently, ITO crystalline particles fabricated utilizing the combination may have identical properties and high crystallinity, and exert dominant electrical properties. Then, electrical conductivity of the ITO crystallites was also studied in the present work.

2. Materials and methods

2.1. Materials

The reactants to produce the seed nanoparticles were indium (III) chloride tetrahydrate ($InCl_3{\cdot}4H_2O$) (>99.95%), tin (IV) chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) (>98.0%) and sodium hydroxide solution (NaOH) (1 M). To fabricate ITO nanoparticles, $InCl_3{\cdot}4H_2O$, $SnCl_4{\cdot}5H_2O$ and urea (>99.0%) were used as an indium source, a tin source and a precipitation-inducer to produce an indium compound and a tin compound, respectively. All chemicals were purchased from Kanto Chemical Co., Inc., and used as received. Water that was ion-exchanged and distilled with Shimadzu SWAC-500 was used in all preparations. The water was deaerated by N_2 gas-bubbling before use in all experiments.

2.2. Methods

2.2.1. Preparation

A colloid solution of seed nanoparticles was synthesized using a coprecipitation process with indium ions, tin ions and a base. An aqueous solution of NaOH was added to an aqueous solution of $InCl_3$ and $SnCl_4$ with vigorous stirring at room temperature (ca. 25 °C). The reaction time was 8 h. The initial In/Sn and NaOH concentrations were 0.009 M/0.001 M and 0.035 M, respectively. The seed nanoparticles were washed by repeated centrifugation, supernatant removal via decantation, water addition and sonication. This procedure was repeated three times. To obtain a concentrated seed nanoparticle colloid solution, the amount of added water was reduced by 1/10, which resulted in concentrations of 0.09 M In and 0.01 M Sn in the final colloid solution.

Precursor particles for ITO were fabricated using the homogeneous precipitation method. The seed nanoparticle colloid solution and a urea aqueous solution were added to a freshly prepared aqueous solution of $InCl_3$ and $SnCl_4$ at room temperature. The mixture was stirred at 80 °C for 8 h. The initial concentrations were 0.00018 M/0.00002 M for In/Sn derived from the seed solution, 0.09 M/0.01 M for In/Sn derived from the freshly prepared solution and 1.55 M for urea, which resulted in a seed content of 2 wt% with respect to the final ITO. The particles in the mixture were washed by repeated centrifugation, supernatant removal via decantation, water addition and sonication. This procedure was repeated three times. To obtain ITO particle powder, the residue at the bottom of the centrifuge tube after the supernatant removal via decantation was dried in vacuo at room temperature to form a powder, which was subsequently annealed in air at 500 °C for 2 h (s-ITO). For comparison, two other types of ITO particles were fabricated from precursor particles. One precursor was particles fabricated using the homogeneous precipitation method without the seed nanoparticles. The other one was the seed nanoparticles in the seed nanoparticle colloid solution. The ITO particle powders (n-ITO and c-ITO, respectively) were obtained from the above-mentioned as-prepared precursor particles, using the identical procedure as that for the ITO that was fabricated with the homogeneous precipitation method.

2.2.2. Characterization

The particles were characterized using transmittance electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffractometry (XRD). The TEM was performed using a JEOL JEM-2000FX II microscope at 200 kV. The TEM samples were prepared by dropping and evaporating the particle suspensions onto a colloid-coated copper grid. The SEM was performed using a Hitachi S-4300 microscope at 15 kV. The XRD patterns of the particle powder samples were obtained with a Rigaku Ultima IV X-ray diffractometer at 40 kV and 30 mA with CuKα radiation (λ: 0.154056 nm).

The volume resistivities of the particle powders were measured using a 4-pin probe to determine the electrical resistivity of the particles. Because ITO reduction is a conventionally performed procedure to make the ITO electro-conductive, the reduction procedure was also performed in the present work. The powder was reduced by annealing in H_2/N_2 gas prior to the measurement. The measurements were performed while applying pressure to 2 g of the powder sample in a pressing die set with a diameter of 2.5 cm in the range of 0–300 kg-f/cm^2 using a Mitsubishi Chemical Analytech MCP-T610 resistivity meter.

3. Results and discussion

3.1. Morphology of seed nanoparticles

The inset of Fig. 1 shows a TEM image of the seed nanoparticles. The particle shape was a rectangular parallelepiped, and the particles had an average longitudinal size of 62.2 ± 21.6 nm and a lateral size of 26.2 ± 9.9 nm. Fig. 1 shows an XRD pattern of the seed particles. Several peaks were clearly detected at 22.4°, 31.8°, 39.2°, 51.4°, 56.7°, 66.5°, 71.1° and 75.7°, which correspond to *d*-values of 0.397,